COLOPHON

The attached paper has little connection with my current research in Computer Science and Digital Documents. It is another in a series of experiment to see how long it would take me to build an electronic versions of my early published papers.

This one appeared in the journal "Molecular Physics" (Taylor & Francis) in 1970.

The paper was scanned in to Omnipage OCR from a an original offprint. UNIX *troff* was used to set up the correct typeface (Times) and to get the line and page breaks as accurate as possible. Specialist material within the paper was re-set with the *eqn*, *tbl* and *psfig* pre-processors for *troff*.

The two diagrams were also scanned in from the original offprint of the paper, cleaned up in Adobe Photoshop and then vectorized using Adobe Streamline. Further small adjustments were performed in Adobe Illustrator before exporting each diagram to version 3.2 of Illustrator's Encapsulated PostScript (but with no TIFF preview). This Encapsulated PostScript was then incorporated into the paper using *psfig*.

This form of "rescue" of an early paper can produce a very pleasing result but the time taken to do it (10 hours for this paper) makes it prohibitively expensive for any publisher to undertake as a general procedure, especially given that you need to be totally familiar with something like *troff*/*eqn*, or LaTeX before you can even begin. The vast majority of the time taken for this paper was in re-setting the mathematics and the tables (particularly the two tables in landscape mode).

The "Molecular Physics" home page is at:
`http://www.tandf.co.uk/journals/titles/00268976.asp`
and PDF versions of more recent papers in that journal (i.e. from vol. 87,1996, onwards) are available via that site.

Calculated ionization potentials of the linear alkanes

by D. F. BRAILSFORD AND B. FORD

Department of Mathematics, University of Nottingham, University Park, NOTTINGHAM NG7 2RD, England

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The equivalent orbital (EO) method is investigated and used for predicting outer and inner ionization potentials of the linear alkanes. The calculated ionization potentials are in good agreement with those observed in photoelectron spectra provided that a set of 12 parameters is used in the theory. An optimization technique is used to find the best values for thle parameters and a single transferable parameter set can be found which is applicable to all the n-alkanes. A good fit to the experimental results can only be obtained if the uppermost molecular orbital of the n-alkanes is an antisymmetrical orbital built up from CH equivalent orbitals.

1. Introduction

Recent advances in molecular photoelectron spectroscopy have made possible a more rigorous test of an elegant method for calculating the ionization energies of a molecule proposed by Hall and Lennard-Jones [1, 2]. The method depends on the fact that a single determinant is invariant to a unitary transformation and thus one can always pass from an equivalent orbital basis to a molecular orbital basis in the solution of a particular problem. The equivalent orbital basis gives a classical localized picture of a molecule. It is readily parameterized in terms of bond self-energy and bond-bond interactions. The molecular orbital basis gives an overall picture of the whole molecule, which is essential for consideration of properties such as molecular ionization potentials. Hence, starting with a parameterization of the equivalent orbital basis of the self-consistent hamiltonian, the ionization potentials of the molecule and related molecular orbitals are given by the eigenvalues and eigenvectors of the hamiltonian matrix equation. Hall's method has the further advantage of being an accurate solution of the SCF equations. In a highly symmetrical molecule or in a molecule containing only a limited number of chemically equivalent bonds, the number of different matrix elements will be small. Further, because of the bond localization inherent in the model, bond self-energy and bond-bond interaction parameters are transferable throughout a homologous series. In Hall's method the parameters are determined from the experimentally known first ionization potentials of a series of molecules.

2. The Hall Method

The matrix elements in an orthonormal equivalent orbital (EO) basis $\{\chi_i\}$ are given by:

$$e_{mn} = \int \bar{\chi}_m H_{\mathrm{SCF}} \chi_n \, d\tau.$$

Hence if two equivalent orbitals χ_m and χ_n bear the same relation to each other as do

another pair χ_p and χ_q then

$$e_{mn} = \int \bar{\chi}_m H_{\mathrm{SCF}} \chi_n \, d\tau = \int \bar{\chi}_p H_{\mathrm{SCF}} \chi_q \, d\tau = e_{pq}.$$

Now

$$\psi_i = \sum_l \chi_l T_{l\,i} \, ,$$

where the $\{\psi_i\}$ are a molecular orbital (MO) basis. We can write:

$$\begin{aligned} E_{ij} &= \int \bar{\psi}_i H_{\mathrm{SCF}} \psi_j \, d\tau \\ &= \int \sum_m \chi_m \, T_{im}^{-1} H_{\mathrm{SCF}} \sum_n \chi_n \, T_{nj} \, d\tau \\ &= \sum_{m,\,n} T_{im}^{-1} \, e_{mn} \, T_{nj} \, . \end{aligned}$$

For molecular orbitals we require:

$$E_{ij} = \delta_{ij} \varepsilon_i,$$

where, by Koopmans' theorem [3], the ε_i represent vertical ionization potentials.

Thus

$$\sum_{m,\,n} T_{im}^{-1} \, e_{mn} \, T_{nj} = \delta_{ij} \varepsilon_i$$

or

$$\sum_n e_{mn} T_{nj} = e_j T_{mj}.$$

Hence the eigenvalues determined by this equation are the required vertical ionization potentials, and the eigenvectors are the molecular orbitals.

3. Parameterization

3.1. Geometry

The 'staggered' configuration is known to be energetically preferred in ethane and it has been assumed throughout that the staggered linear configurations will similarly be preferred for the other *n*-alkanes. Hence, the point group of methane is T_d, of ethane D_{3d}, of propane, pentane, heptane, nonane C_{2v}, and of butane, hexane, octane, decane C_{2h}. All the ionization potentials of the molecule are calculated and all bond--bond interactions up to 2.505 Å separation are included. Nearest neighbour bond interactions have been written in the form ( )−( ), second neighbour interactions as ( )$_\wedge$( ) and all longer range interactions as ( )( ). The required parameters are listed below together with examples of the interactions involved, e.g. (1 → 1). The numbers in brackets refer to the bond numbering for *n*-butane (figure 1).

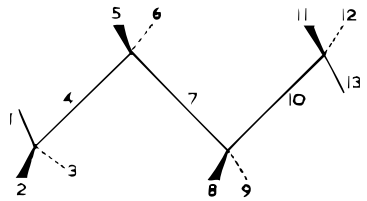

Figure 1. Bond numbering in the *n*-butane molecule.

a The C–H bond self-energy (1 → 1).
b The (C–H)–(C–H) nearest neighbour bond-bond interaction (1 → 2).
c The C–C bond self-energy (4 → 4).
d The (C–H)–(C–C) nearest neighbour bond-bond interaction (1 → 4).
e The (C–C)–(C–C) nearest neighbour bond-bond interaction (4 → 7).
f The $(C–H)_{\wedge}(C–H)$ hidden second neighbour bond-bond interaction (2 → 6).
g The $(C–H)_{\wedge}(C–H)$ direct second neighbour bond-bond interaction (1 → 5).
r The $(C–H)_{\wedge}(C–C)$ hidden second neighbour bond-bond interaction (1 → 7).
s The $(C–H)_{\wedge}(C–C)$ direct second neighbour bond-bond interaction (2 → 7).
y The $(C–C)_{\wedge}(C–C)$ hidden second neighbour bond-bond interaction (4 → 10).
t The (C–H)(C–H) direct space bond-bond interaction (2 → 8).
u The (C–H)(C–H) diagonal space bond--bond interaction (2 → 9).

3.2 First set of parameters

Estimates of *a* and *b* can be derived [1] from the known experimental vertical ionization potentials of methane [4]. This gives:

$$a - b = -13.7,$$
$$a + 3b = -23.1,$$
$$a = -16.05, \quad b = -2.35$$

A small change in the length of the C-H bond is found between ethane and methane [5]. In acquiring a first estimate of the parameters this is ignored. The experimental ionization potentials of ethane [4] give estimates of *c*, *d*, *f* and *g* [l]:

$$a - b + f - g = -12.0,$$
$$E_1 = -13.1,$$
$$a - b - f + g = -15.2,$$
$$a + 2b - f - 2g = -20.4,$$
$$E_2 = -24.2,$$

where E_l, E_2 are the roots of

$$\begin{pmatrix} c - E & d\sqrt{6} \\ d\sqrt{6} & a + 2b + f + 2g - E \end{pmatrix}$$

Thus, if $a = -16.05$ then $b = -2.45$, $f = 0.88$, $g = -0.72$, $c = -15.8$. *c* is found by equating the trace of the equivalent orbital matrix to the sum of the experimental ionization potentials. Hence it contains the summed experimental error and is the least reliable of the parameters to date. *d* can now be calculated from the determinant yielding $d = -1.945$.

The assignment of the various ethane I.P.'s set out above presumes the following electronic structure for the uppermost 14 electrons in the ethane molecule:

$$(2a_{1g})^2(2a_{2u})^2(le_u)^4(3a_{1g})^2(le_g)^4.$$

This is in accordance with recent experimental evidence [4].

[PROPANE 5]		[PROPANE 11]		[BUTANE 12]		[PENTANE 12]	
Optimized parameters	Calculated I.P.'s (eV)	Optimized parameters	Calculated I.P.'s (eV)	Optimized parameters	Calculated I.P.'s (eV)	Optimized parameters	Calculated I.P.'s (eV)
a –16. 05†	–11.30*	*a* –16.02	–11.35*	*a* –15.97	–10.96*	*a* –15.77	–10.67*
b –2.45†	–11.-95*	*b* –2.43	–12.25*	*b* –2.49	–11.60*	*b* –2.45	–11.62*
c –15.80†	–12.32*	*c*– 16.40	–12.53*	*c* –15.92	–12.38	*c* –16.46	–12.05*
d –1.94†	–13.66*	*d* –1.87	–13.65*	*d* –1.89	–12.63	*d* –1.87	–12.12
e –1.26	–14.08*	*e* –1.43	–14.27*	*e* –1.34	–13.51	*e* –1.31	–13.13
f 0.88†	–14.90*	*f* 0.86	–15.23*	*f* 0.92	–13.66	*f* 0.91	–-13.51
g –0.72†	–15.83*	*g* –0.70	–15.77*	*g* –0.70	–14.38	*g* –0.71	–13.83
r 0.89	–19.42*	*r* 0.93	–19.41	*r* 1.00	–14.95	*r* 1.01	–14.00
s –0.39	–22.21*	*s* –0.37	–22.20*	*s* –0.40	–16.20*	*s* –0.41	–14.87*
t –0.21	–24.32*	*t* –0.19	–24.30*	*t* –0.34	–19.40*	*t* –0.39	–15.14
u –0.26		*u* –0.25		*u* –0.23	–20.46	*u* –0.25	–16.29*
				y –0.90	–22.59	*y* –0.02	–19.22
					–24.74		–19.33
							–21.29
							–23.19
							–24.79

† These parameters are not being optimized.
* I.P.'s being used in the fitting process

Table 1. Optimized parameters and calculated ionization potentials for propane, *n*-butane and *n*-pentane.

3.3. Optimization procedure

The standard direct search procedure BEST UNIVAR [6] was employed for optimization. Given an estimated set of data and an order of parameter analysis, BEST UN1VAR proceeds to find the minimum of a given functional by first conducting a search employing one-at-a-time variation of each parameter, and then, if these searches lead to a functional minimum lower than the initial functional value, a pattern move is applied, involving all parameters. These two distinct approaches are used in turn until the absolute minimum of the functional is found. In the present problem the functional used was the sum of the squares of the differences between the calculated and experimental vertical ionization potentials for each particular alkane or group of alkanes.

3.4. Results from five sets of parameters

For the first parameterization of propane [PROPANE 5] the parameters *a*, *b*, *c*, *d*, *f* and *g* were determined in the manner described in §3.2. The optimum values

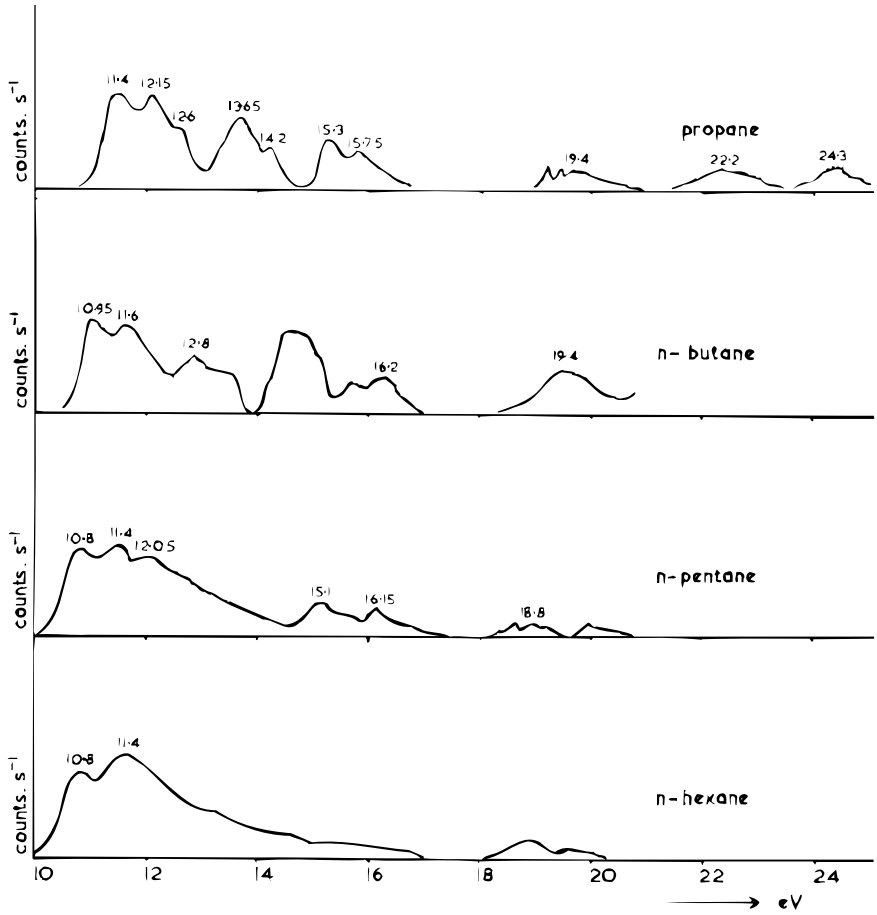

Figure 2. Photoelectron spectra of propane, *n*-butane, *n*-pentane and *n*-hexane (courtesy of Professor W. C. Price). Values of vertical I.P.'s used in the optimizations are indicated above the appropriate peaks.

of the remaining five parameters *e*, *r*, *s*, *t*, *u* were found using BEST UNIVAR. Next, to test the validity of the model being employed, a programme was written to optimize the full parameter set for propane [PROPANE 11], butane [BUTANE 12] and pentane [PENTANE 12], each molecule being treated separately. Starting values for the parameters were taken from the [PROPANE 5] optimization, and the results of all four optimizations are shown in table 1. The experimental ionization potentials used in the fitting process were taken from recent photoelectron spectra of the *n*-alkanes obtained by Potts and Price [7]. The spectra for propane, *n*-butane, *n*-pentane and *n*-hexane are reproduced in figure 2 (by courtesy of Professor W. C. Price). The values of the vertical ionization potentials used in the various optimizations are indicated above the appropriate peaks of figure 2.

In the case of propane all of the calculated ionization potentials were fitted to the observed values. For butane and pentane the individual ionization potentials are much more difficult to pick out but identification of some of the inner levels is aided by the break in the spectra between approximately 16.5 and 18 eV corresponding to the gap in orbital energies between 2*p* and 2*s* electrons. Consequently only four prominent peaks could be fitted in butane and five in pentane. All ionization potentials (I.P.'s) used in the various fittings are marked with asterisks in table 1.

It is pleasing to note the similarity of parameters between [PROPANE 5] where six parameters were held constant and [PROPANE 11] where all parameters were allowed to vary. The only strong change in value was for the *c* parameter, and this could have been predicted from considerations in §3.2. Indeed, the sets of optimized parameters obtained for the four cases shown in table 1 are all markedly

	Calculated I.P.'s			
'Best compromise' parameters	Propane	*n*-butane	*n*-pentane	*n*-hexane
a −15.92	−11.24*	−10.93*	−10.76*	−10.66*
b −2.43	−12.08*	−11.77*	−11.85*	−11.48*
c −16.33	−12.40*	−12.45	−12.02*	−11.87
d −1.87	−13.44*	−12.76	−12.13	−12.41
e −1.31	−14.25*	−13.61	−13.42	−12.71
f 0.88	−15.19*	−14.04	−13.44	−12.72
g −0.73	−15.79*	−14.44	−13.80	−13.63
r 0.98	−19.33*	−15.11	−14.18	−14.08
s −0.45	−21.97*	−16.14*	−15.08*	−14.14
t −0.36	−24.32*	−19.23*	−15.32	−14.36
u −0.31		−20.25	−16.33*	−15.38
y −1.03		−22.46	−19.02	-15.49
		−24.99	−19.35	−16.46
			−21.10	−18.73
			−23.13	−19.37
			−25.41	−19.88
				−21.80
				−23.63
				−25.73

Table 2. Simultaneous fitting of I.P.'s marked (*) in propane, *n*-butane, *n*-pentane and *n*-hexane [SIMOPT 12].

Sym. species (C_{2v})	Orbital energy (eV)	Molecular orbital
b_2	−11.24	$0.3516(h_3-h_2+h_9-h_8)+0.5027(h_5-h_6)$
a_1	−12.08	$0.2570(h_2+h_3+h_8+h_9)+0.3174(h_5+h_6)-0.3604(h_1+h_{10})-0.3705(c_4+c_7)$
b_1	−12.40	$-0.1246(h_2+h_3-h_8-h_9)+0.5266(h_1-h_{10})-0.4378(c_4-c_7)$
a_2	−13.44	$0.5000(h_3-h_2+h_8-h_9)$
b_1	−14.25	$-0.3459(h_2+h_3-h_8-h_9)+0.2195(h_1-h_{10})+0.4610(c_4-c_7)$
a_1	−15.19	$-0.0738(h_2+h_3+h_8+h_9)+0.2343(h_5+h_6)+0.5188(h_1+h_{10})-0.4063(c_4+c_7)$
b_2	−15.79	$0.3555(h_2-h_3+h_8-h_9)+0.4973(h_5-h_6)$
a_1	−19.33	$0.3061(h_2+h_3+h_8+h_9)-0.5009(h_5+h_6)+0.1759(h_1+h_{10})-0.1755(c_4+c_7)$
b_1	−21.97	$-0.3388(h_2+h_3-h_8-h_9)-0.4178(h_1-h_{10})-0.3096(c_4-c_7)$
a_1	−24.32	$0.2912(h_2+h_3+h_8+h_9)+0.3057(h_5+h_6)+0.2648(h_1+h_{10})+0.4084(c_4+c_7)$

Table 3. Molecular orbitals of propane derived from the [SIMOPT 12] parameter set. c_4 c_7 are CC EO's. h_1, h_2, h_3, h_5, h_6, h_8, h_9, h_{10} are CH EO's.

similar to one another, and the calculated ionization potentials agree very well with the experimental values shown in figure 2.

Since the parameters obtained in these individual optimizations were very similar it was clear that a single transferable set of parameters could be found for all the linear alkanes. This 'best compromise' set [SIMOPT 12] was obtained by simultaneously fitting all the ionization potentials marked by asterisks in table 1, together with the first two ionization potentials of *n*-hexane taken from the photoelectron spectrum (figure 2). The results are shown in table 2, and comparison with the photoelectron spectra shows that a large number of the ionization potentials can be predicted simultaneously from a single set of parameters. For the sake of consistency only alkanes up to *n*-hexane, for which photoelectron spectra are available, have been considered here. For most of the alkanes beyond *n*-hexane only the first I.P.'s are available. Nevertheless, these can be predicted quite successfully using the [SIMOPT 12] parameter set.

The calculated ionization potentials were found to be very insensitive to variation of the y parameter, which is required for all the *n*-alkanes beyond butane. Consequently values quoted for y are highly inaccurate and this parameter may be kept at zero without substantially affecting the calculated ionization potentials or molecular orbitals. The parameters f and r, like y, are 'hidden interaction', parameters. It can be seen from figure 1 and §3.1 that r is similar in nature to y, but occurs only at the ends of the straight chain. Thus, although the propane I.P.'s depend strongly upon r because the chain length is short, the importance of r becomes less pronounced as chain length increases. The f interaction, by contrast, is associated with every carbon atom of the chain and is fundamental to all calculations.

The molecular orbitals of propane, obtained from the [SIMOPT 12] parameters are shown in table 3 together with the symmetry species of the various orbitals. The MO's are expressed as combinations of the various EO's. The EO's centred on the two C–C bonds of propane are called c_4 and c_7. The EO's on the C–H bonds of the two terminal methyl groups are h_1, h_2, h_3 and h_8, h_9, h_{10}, and the EO's on the C–H bonds of the central CH_2 group are h_5, h_6.

It can be seen that the uppermost antisymmetrical molecular orbital is of type b_2 and is localized over the CH bonds.

4. Discussion and conclusions

It is apparent from the foregoing sections that the EO method can be employed to predict all the ionization energies of a linear alkane using a single transferable set of parameters. It is also clear that the 'long range' parameters in the present theory will be very sensitive to the geometry of the molecule. The staggered configuration of the alkanes has been presumed in all the calculations described. A further calculation was performed for the eclipsed configuration of propane. The nature of the long range interactions is radically altered here but optimization of all the relevant parameters did not give a good fit to the observed I.P.'s in the photoelectron spectrum (figure 2). This confirms, we believe, that the staggered configuration is a better approximation to the true geometry of propane than the eclipsed form.

Previous EO calculations for the linear alkanes [1, 8, 9] were not based on sufficient experimental evidence to decide the true nature of the uppermost MO of the alkanes. Indeed, Hall [8] concluded that this orbital could be either an

antisymmetrical CH MO or a symmetric orbital localized mainly over the CC bonds. Both of these hypotheses agreed with the experimental evidence available at that time. Table 3 shows that in the present work the uppermost orbital of propane is built up only from CH EO's. This behaviour maintains for all the linear alkanes studied. Recent experimental observation [4] of vibrational fine structure, corresponding to the CH deformation, on the first peak of the ethane photoelectron spectrum, lends weight to this result. however, many studies of the alkane molecular ions using the EO method have assumed the uppermost orbital to be a symmetric CC MO [1, 9]. It is interesting to note that this type of molecular orbital will only be uppermost if a truncated set of parameters (*a*, *b*, *c*, *d*, *e*) is used and all longer range interactions neglected. Lorquet has shown that the first ionization potentials of the linear alkanes can be adequately predicted using this smaller set of parameters [9].

The full 12 parameter sets used in this work were most successful in predicting the inner ionization potentials now available from the photoelectron spectra. However, a trial calculation was performed using only the five parameter set *a*, *b*, *c*, *d*, *e*. An F test showed clearly that the fitting of the I.P.'s obtained in this way was very much worse than when the extended set of parameters was used. The chief objection to the five parameter set is that insufficient flexibility exists to lift the multiple degeneracies that occur in the calculated I.P.'s. When a larger set of parameters is used these accidental degeneracies are lifted, but genuine orbital degeneracies, if any, remain. This makes the identification of the symmetry species of the various orbitals very much simpler. Occasionally one sees a splitting of orbital degeneracy in photoelectron spectra [4] largely due to Jahn-Teller and spin-orbit coupling effects. The former effect is due to a change in molecular geometry on ionization and could not be accounted for in the present theory, which presumes a fixed molecular framework.

The method we have used presumes that Koopmans' theorem is valid. This is not always so, for ε_i values obtained from *ab initio* calculations often deviate considerably from experimental I.P.'s. Two sources of error are immediately apparent in the present calculation. The first, is the presumption that orbitals which are self-consistent for the molecule are also self-consistent for the ion. Errors due to this assumption can be shown to be small [9]. The second is the inevitable neglect of electron correlation effects in any one-electron formulation. This latter effect can be allowed for by means of an extension to Koopmans' theorem involving a polarizability correction term [10]. This correction will also be small due to the low polarizability of the alkanes. It is also fortunate that the two effects mentioned tend to cancel [11].

Thus the EO method, like all other semi-empirical methods, will inevitably work best when a related series of molecules is considered. However, the new experimental evidence from photoelectron spectra will make parameterization of the theory and the identification of orbital symmetry species very much easier.

We should like to thank Professor W. C. Price, F.R.S., for much valuable correspondence and for so freely communicating many of his results prior to publication. Thanks are due to Professor G. G. Hall for his continued interest in this work and for many useful discussions, and to the Director and Staff of the Cripps Computing Centre of Nottingham University for their usual efficient service and much computing time.

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